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"COMBUSTION CHARACTERISTICS OF CRYSTALLINE ROCKET OXIDIZERS"

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"COMBUSTION CHARACTERISTICS OF CRYSTALLINE ROCKET OXIDIZERS"

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I. Abstract

This report describes a combustion research and testing program that has achieved one of its long range goals; that of providing new theory and practice for burning rate control of solid rocket propellants. In addition, new understanding has been added of the role played by the crystalline oxidizers used in those propellants.

Chemical and physical modifications were made to the most widely used crystalline oxidizer: ammonium perchlorate. Mass spectrometer, DTA and combustion tests were run. The intent was to learn about, and then to control combustion mechanisms; that is to: increase or decrease burning rate, promote easier ignition, improve safety and storage life and to beneficially affect quenching and restart capabilities.

The fundamental combustion property studied was the single crystal burning rate. This was then related to the burning of oxidizer powders. A simple screening test was developed that allowed the rapid determination of powder burning rates on a routine basis for all monopropellant (self-sustaining combustion) oxidizers. This test showed that there was a wide range of burning rates available for study when chemical and physical modifications were made to the basic control oxidizer; ammonium perchlorate. Burning rates ranged over 1000 fold, from 0.02 in/sec for the slowest burning powders at atmospheric pressure, to about 20 in/sec for A.P. at 100 atmospheres.

Thermodynamic calculations were made to determine the adiabatic combustion temperature and final combustion products for

the monopropellant burning conditions at several pressures.

Time-of-flight and high resolution mass spectral studies were run at temperatures of 80°C to 165°C and 70 ev. electron bombardment to get indications of the kinds of transitory species that might be present in the very earliest stages of combustion.

It was found that ClO , ClO_2 , ClO_3 , and HClO_4 along with NH_4 , ammonia, and NH_2 fragments are products of primary decomposition, that are not found as final combustion products.

To correlate laboratory tests with actual state-of-the-art propellant burning rates, one of the fastest burning oxidizers prepared, methyl ammonium perchlorate (MAP), was substituted for one-fourth of the ammonium perchlorate in a typical fast burning propellant. This modified formulation gave a burning rate more than twice that of the control, and significantly higher than the fastest burning propellants using the best iron catalysts now known. The typical catalyzed high burning rate propellant has a rate of about 2 in/sec at 2000 psia. The propellant prepared with MAP, and with no catalyst, gave a burning rate of 2.75 in/sec.

In MAP, as compared with AP, there are nearly twice as many oxidizable atoms brought into intimate contact with the powerful chlorine oxide species.

It is theorized that the MAP-containing propellant, which has no higher flame temperature nor finer particle sizes than the controls, burns faster than even the catalyzed controls because the flame temperature is brought much closer to solid surfaces.

This closer flame zone allows greater heat conduction back to the surface, thereby causing faster burning rates.

II. Introduction

A fundamental understanding of the spectrum of combustion characteristics of crystalline oxidizers is important if complete knowledge pertaining to the combustion and stability characteristics of composite solid propellants is to be attained. This research is increasing that understanding. It involves theoretical and experimental studies of the burning of crystalline oxidizers, and the combustion dynamics of their interaction with other propellant ingredients.

One particular research quest has received considerable attention over the past two decades: finding the key to practical burning rate control of solid propellants. It has been generally believed that there must be some relatively simple and effective means of halving or doubling the burning rate of a practical propellant. Effective catalysts have been sought. Iron and chromium compounds have been found to be particularly effective. It has also been felt that the crystalline oxidizer exercises far more control over the propellant burn rate than the fuel binder or the metal powder fuel. In the past it was not possible to increase burning rates far beyond that allowed by A.P.; nor decrease them far below that allowed by ammonium nitrate. This research program has specifically sought to explain why this was so. We have also sought to study only effects in the combustion of crystalline oxidizers that would be

directly translatable to modern high energy rocket propellants. By culminating each phase of laboratory and theoretical studies with actual propellant combustion tests we have demonstrated the soundness of the approach.

Several fundamental aspects of the combustion of pure oxidizers have been determined by the combined research efforts of the University of Delaware and other groups. We have determined both single crystal and powder burning rates for ammonium perchlorate as a function of pressure. We also have prepared a variety of related compounds which closely approximate in their fuel/oxidizer balance the range of compositions used in real propellants. Single crystal and powder samples were supplied to Air Force, Navy, Army and NASA labs in connection with a wide range of fundamental propulsion studies. We know the phase changes these crystals go through and their temperatures. For the conditions of monopropellant combustion, we have calculated the ultimate gas compositions and their adiabatic flame temperatures.

We have shown that a ten-fold change in burning rate can be achieved by changing the anions and cations in crystalline oxidizers. Our studies have specialized in alkyl substitutions to NH_4^+ . Impact sensitivity was found to be directly related to the energy available for release on combustion for a given family of oxidizers. Perchlorates generally had faster burning rates than nitrates, and over limited ranges, the higher adiabatic flame temperature compounds had faster burning rates. Oxidizers with burning rates half as fast as A.P. on the one hand, and six times as fast on the other hand, were discovered. The potential influence of factors such as the cation

base strength were pointed out. Burning of carefully sized and packed oxidizer granules in sample tubes was shown to be a simple and practical screening test to determine relative burning rates.

Further definition and interpretation of the relationships between oxidizer chemical structure and combustion has been given. With the large number of oxidizers available for study, we can vary flame temperatures while making only minor chemical changes, and on the other hand, make fairly significant chemical changes while maintaining the flame temperature. The importance of perchloric acid in A.P. combustion has been clarified by attempting to burn more compounds that cannot form perchloric acid by decomposition. These tests were compared and contrasted with tests of nitrates that could break down to form nitric acid -- and those that could not.

Preliminary analysis has been made of the importance of radiation from the flame zone back to the solid surface of a burning oxidizer. About ten years ago, a study was made of A.P. combustion -- radiation conditions. However, at that time there was not a variety of perchlorate oxidizers available so that radiation mechanisms could be correlated with burning rate. There are only a few regions radiating energy from the flame -- and only a few regions in the solid phase that are able to absorb that radiation. The best matching can thus give the best energy transfer. It is generally believed that conduction from the gas to the solid surface is the chief mode of energy transfer for A.P. burning- or for simple A.P. binder propellants. However, practical propellants containing large quantities of metal oxides in their combustion gases could

materially change this picture.

Studies over the past several years at a number of laboratories in addition to our own, have advanced our state-of-knowledge about shock wave and flame propagation rates through pure single crystals of oxidizers; and through powders of varying bulk density. Although each of these teams specialized in individual aspects of combustion phenomena - many of their results and conclusions have been merged into a unified description of the combustion of the chief ingredient in modern solid propellants. This entire effort has been advanced greatly through study of the excellent microphotography and movies taken by the China Lake group. We now know the monopropellant burning rate of ammonium perchlorate as a function of pressure, we know the phase changes the crystal goes through, their corresponding temperatures, and the initial and probable rate limiting steps of the chemical decomposition. Although the secondary stages of gas phase decomposition and reaction are not yet known - the ultimate gas composition and temperatures are known. We know that multi-micron size dimensions of unimpeded vapor phase normal to a burning crystal surface are necessary for stable combustion.

Confirming the predictions of Maycock, we have found that doping materials added to oxidizers can modify their combustion and stability characteristics greatly. Doping of A.P. with the divalent negative chromate ion increases the monopropellant burning rate. Chemical changes, such as anion and cation substitutions, were shown to cause both increased and decreased combustion rates as compared with A.P. For example, substitution of nitrate for perchlorate- to give ammonium nitrate - gives an oxidizer with a burning rate only

one-half as fast as A.P. When cation changes are made, such as substitution of NH_3OH^+ or N_2H_5^+ for NH_4^+ ; (1) somewhat faster rates are obtained. Most of these changes, tended to lower thermal stability and increase sensitivity to detonation and shock.

The burning rate studies accomplished earlier (2) with crystals and powders gave us standard values and helped to develop standard test techniques so that we would be able to rapidly and economically characterize future oxidizers and propellant additives.

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III. Study Approach: Modifications to Ammonium Perchlorate

As part of a long range plan in 1965, it was determined that alkyl substitutions for the hydrogens in the NH_4^+ cation would provide materials useful in combustion evaluations. It was decided that mono-, di-, and trimethyl ammonium perchlorate should be the starting compounds made after an evaluation of A.P. was completed. DTA data and oxidizer powder burning rates for each compound would be measured, and compared with A.P. as the control. There was little information available in the literature on these compounds. During the early 1900's, there had been two studies (3,4) of a series of alkyl ammonium perchlorates; one concentrating on solubilities - and one on explosion temperatures. Subsequently, there was a U.S. patent issued for methyl ammonium perchlorate as an explosive(5). Our interest was in combustion characteristics of these materials...and no information was uncovered in that area. In 1966, papers were presented by Schmidt and Stammer(6) and by Schmidt (7) on the crystallography, DTA properties and propellant burning rates of several amine perchlorates.

A. Preparation of Substituted Ammonium Perchlorates

The most straightforward and safest method of preparing pure substituted A.P.'s was felt to be the neutralization reaction of amine with perchloric acid in water solution. The amine solutions (methyl, dimethyl and trimethyl) ranged from 40% to 25% by weight in water. The perchloric acid used was 24% by weight in water.

In the preparation of one gram mole of methyl ammonium perchlorate, the dropwise addition of well-stirred dilute HClO_4

produced a maximum temperature rise of 20°C, even with ice bath cooling of 1/2 liter reaction flask.

When reaction was completed, a rotary vacuum evaporator was applied to draw off excess amine and water. The sample was then recrystallized several times from water and dried in a vacuum desiccator. The crystals were rhombic and resembled ammonium perchlorate. The crystal density, measured in methyl polysiloxane was 1.648 g/cc at 20.20°C.

The dimethyl and trimethyl substituted compounds were prepared in essentially the same fashion. The tetra substituted compound was prepared from tetramethyl ammonium hydroxide.

The purified crystals were carefully removed from the final drying watchglasses, and ground in small quantities. The resulting powders were screened to obtain the -40 + 50 mesh (350 micron) fraction and stored in sealed bottles. Methyl A.P. is more hygroscopic than A.P.; and dimethyl A.P. and trimethyl A.P. are less hygroscopic.

B. Differential Thermal Analysis

The most meaningful single analytical test for oxidizer powders was felt to be D.T.A. DuPont Model 900 apparatus was used with a micro sample tube, at a heating rate of 20°C/min., and with glass beads as the thermal reference.

Figure 1 shows the standard D.T.A. thermogram for Ultra High Purity A.P. The single sharp endotherm showing orthorhombic to cubic transition appears at about 240°C. The more complicated exotherm begins gradually at about 300°C. and peaks at about 405°C. At about 430°C there is a second much smaller peak. Less pure samples usually exhibit another broad and lower peak at about 300°C.

Figure 2 (scale compressed by 1/2) for powdered single crystal material, shows nearly the ultimate in purity. Only the final exotherm is present, and it peaks at about 435°C. This indicates a thermal stability far superior to any available grade of A.P.

Figure 3 for methyl ammonium perchlorate shows three distinct endotherms, one at about 40°C. The final exotherm peaks at about 335°C. By analogy with A.P., it is expected that the exotherm could be shifted 50 to 100°C higher with several more recrystallizations.

Figure 4, the thermogram for the dimethyl derivative, shows a peak at about 330°C. Figure 5 for trimethyl A.P. shows three endotherms, like mono methyl, and an exotherm peak at about 305°C.

As will be seen from the data in the following section on pure oxidizer combustion there is no obvious correlation between monopropellant burning rates and DTA thermogram features. We have found, however, that for a given compound those impurities that tend to shift the exotherm to a lower temperature, and to sharpen the exotherm peak, cause faster burning rates.

For precision thermal analyses, giving combined DTA/TGA continuous recording, we prefer the methods of Maycock(8). The additional care and expense in carrying out the Mettler analyses can be well worthwhile in studies where thermal stability comparisons are critical.

FIGURE 1. DTA THERMOGRAM ULTRA HIGH PURITY GRADE AMMONIUM PERCHLORATE
 NH_4ClO_4

SIZE: Micro (3 mm depth)
 REF: Glass bead
 RATE: $20^\circ\text{C}/\text{min}$
 START: 38.3°C
 ATM: N_2
 SCALE: $1^\circ\text{C}/\text{in.}$
 DuPont Model 900

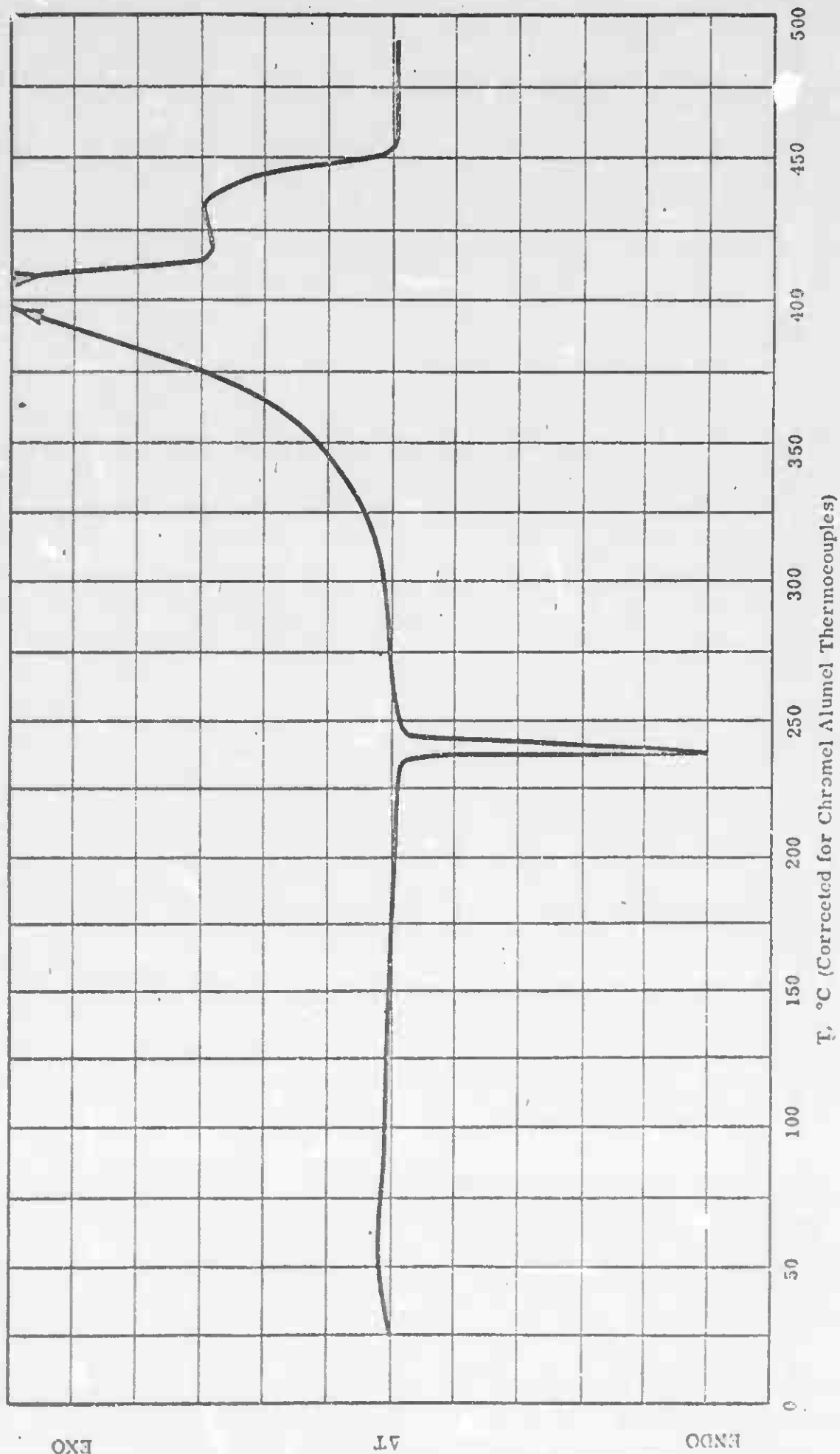


FIGURE 2 DTA THERMOGRAM PURE AMMONIUM PERCHLORATE SINGLE CRYSTAL (POWDERED)
 NH_4ClO_4

SIZE: Micro 3 mm
 REF: Glass beads
 RATE: 20°C/min
 START: 38.8°C

ATM: N_2
 SCALE SETTING: 2°C/in.
 DuPont Model 990

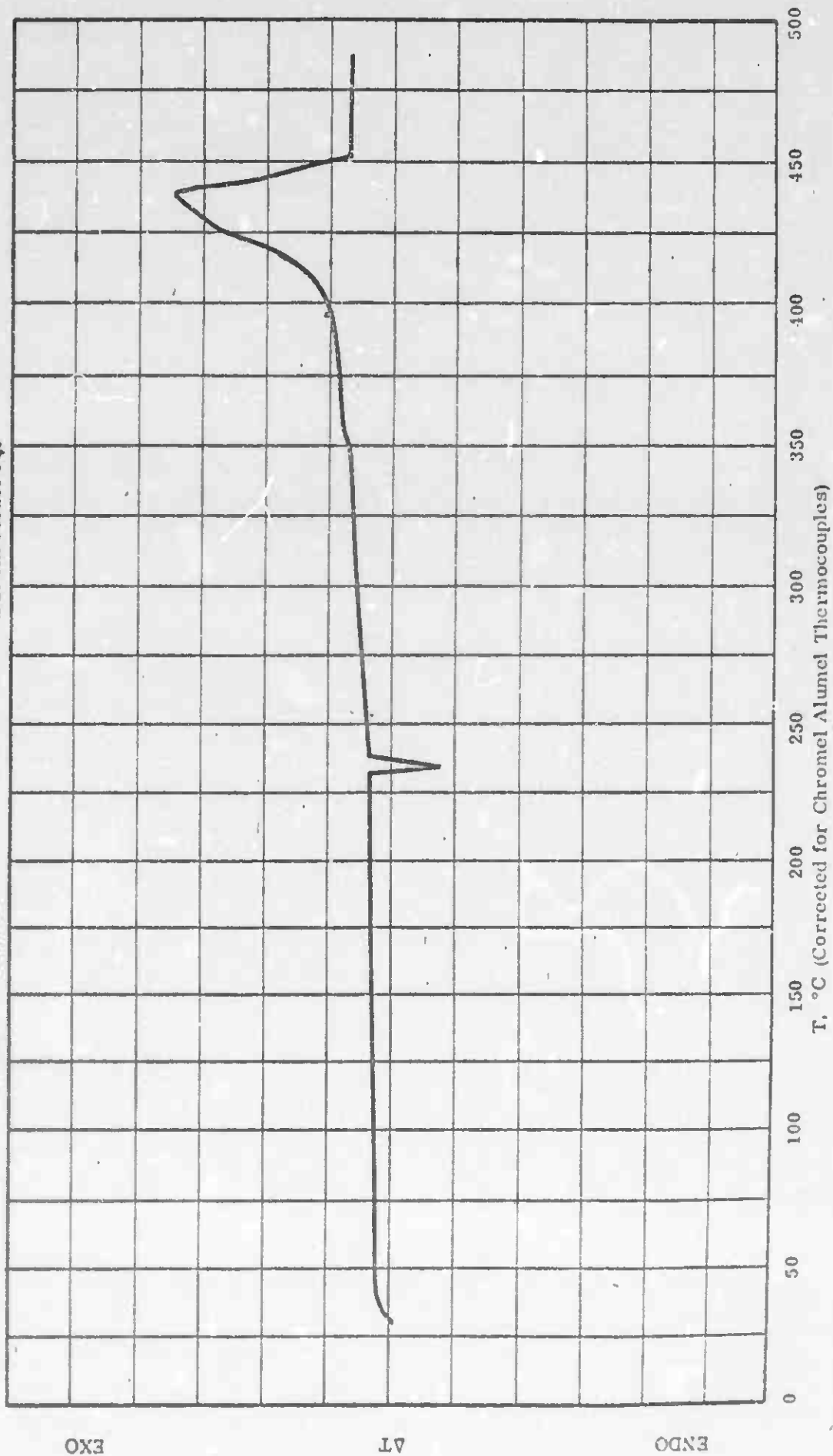


Figure 3 DTA THERMOGRAM MONOMETHYL AMONIUM PERCHLORATE



SIZE: Micro 3 mm depth
REF: Glass beads
RATE: 20°C/min
START: 35.0°C

ATM. N₂
SCALE SETTING: 2°C/in.
DuPont Model 900

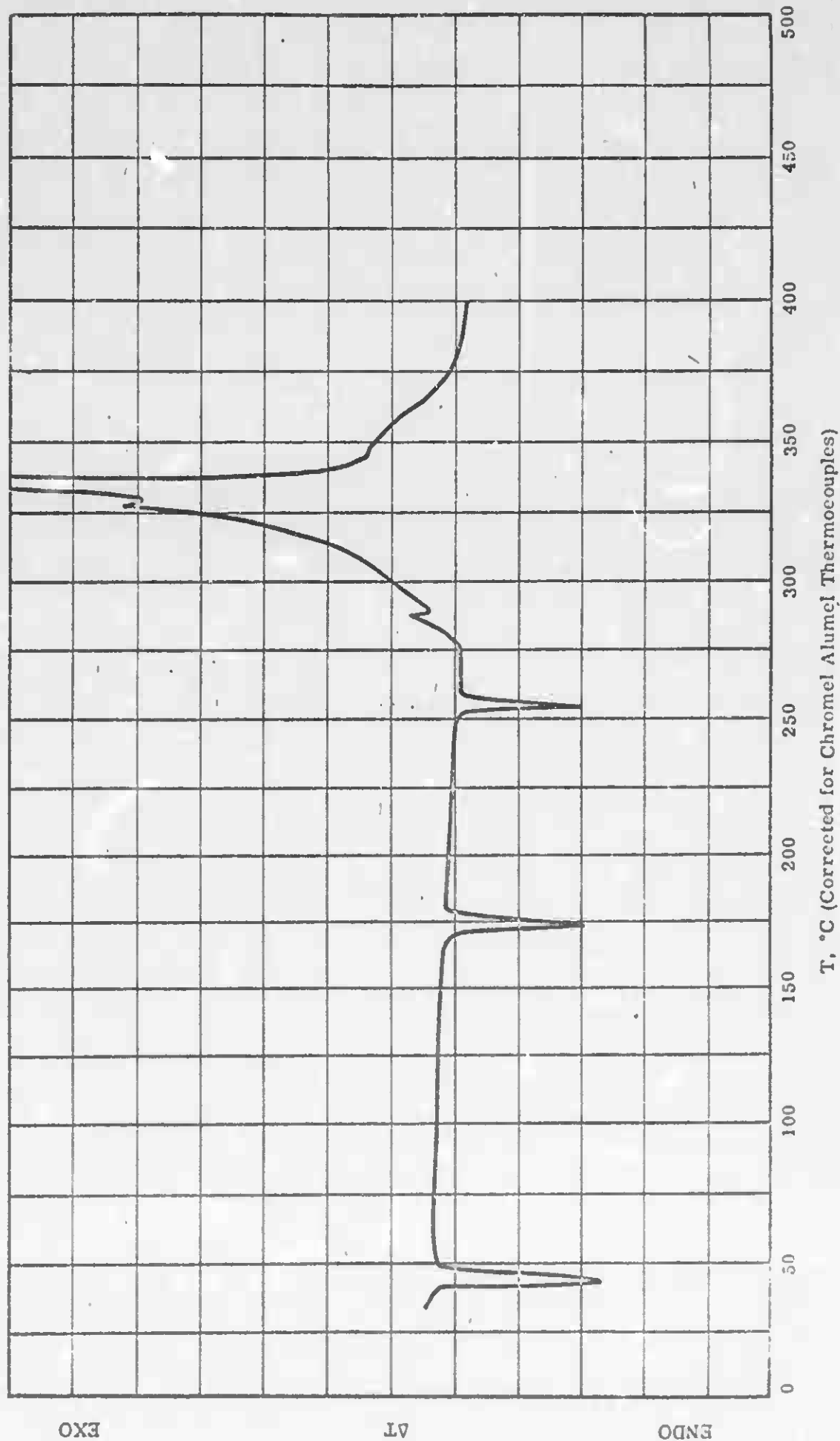


FIGURE 4 DTA THERMOGRAM DIMETHYL AMMONIUM PERCHLORATE
 $(CH_3)_2NH_2ClO_4$

SIZE: Micro 3 mm depth
 REF: Glass beads
 RATE: 20°C/min
 START: 39°C

ATM: N₂
 SCALE SETTING: 1°C/in.
 DuPont Model 900

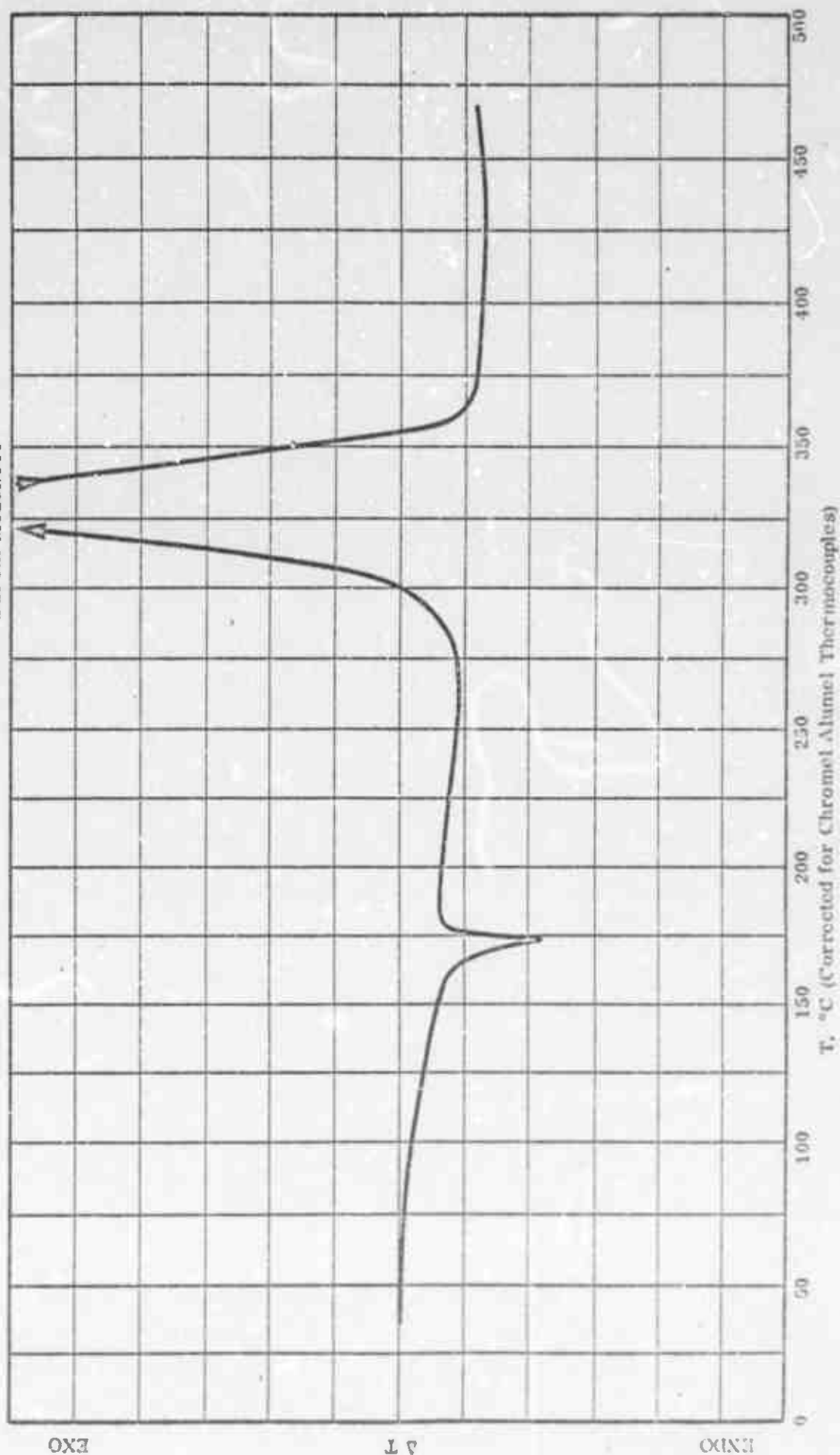
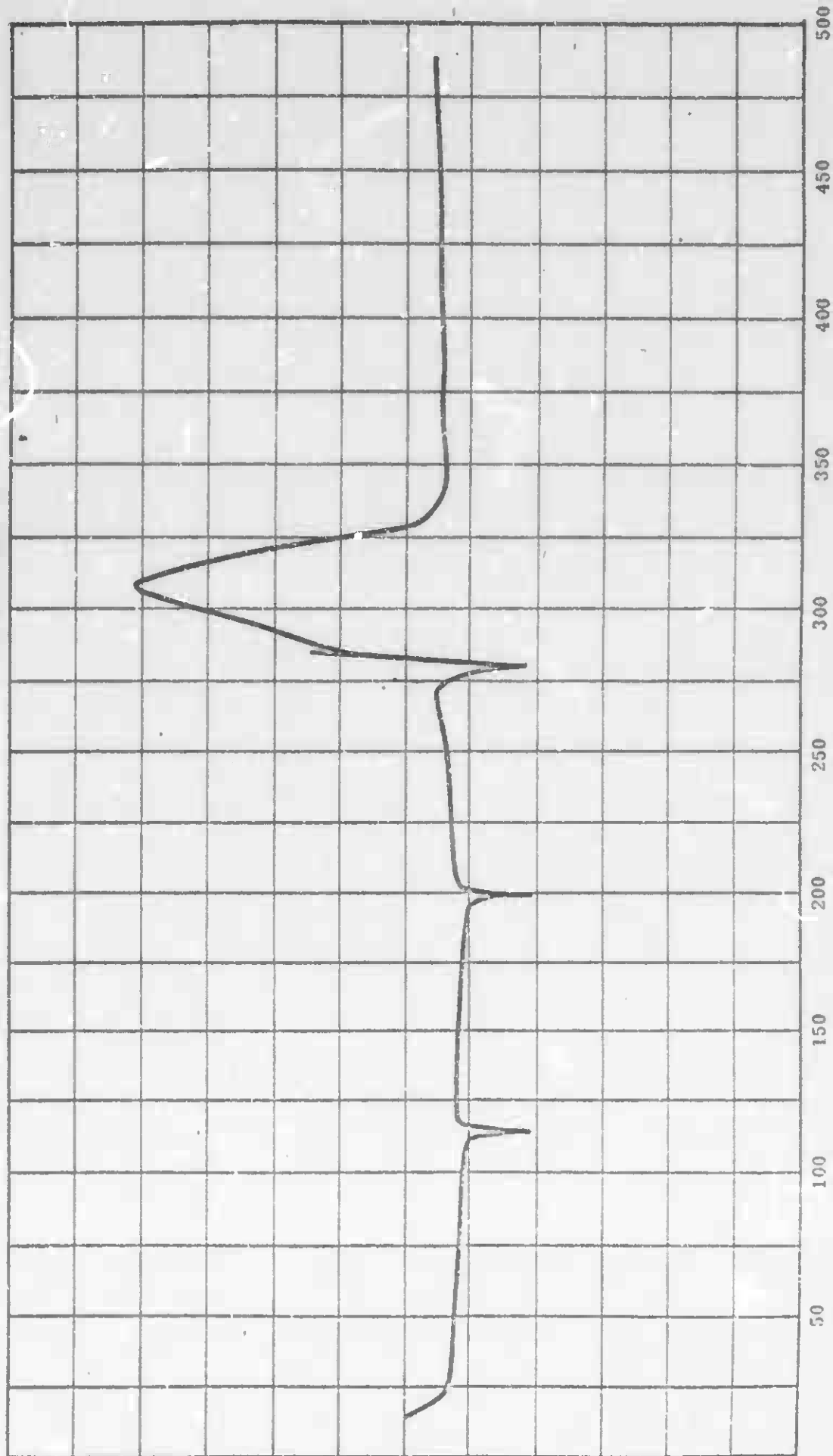


FIGURE 5. DTA THERMOGRAM TRIMETHYL AMMONIUM PERCHLORATE RECRYSTALLIZED, DRIED
 $(CH_3)_3 NClO_4$

SIZE: Micro (3 mm depth)
 REF: Glass beads
 RATE: 20°C/min
 START: 38.1°C

ATM: N_2
 SCALE SETTING: 2°C/in.
 DuPont Model 900



T, °C (Corrected for Chromel Alumel Thermocouples)

IV. Modified Oxidizer Flame Temperatures and Combustion Products.

Over the past ten years we have had ample evidence of the efficiency of computer calculations in telling us such useful parameters as adiabatic flame temperature and the rocket performance figure of merit - specific impulse. There have been a few rough spots here and there when inaccurate heats of formation, inaccurate heat capacity information and programs that didn't allow for certain phase changes or species caused problems. By and large, however, a number of computer programs have been written - and they now check pretty well with each other - and with measured data. The NASA program we use minimizes the free energy of the gas species in an adiabatic combustion reaction. It relies only on the heats of formation and heat capacities of the species it is given. It generates a list of gas product species consistent with the conservation of mass and energy in going from a solid crystal at 298.16°K to equilibrium gas species at the adiabatic flame temperature.

Tables I through V give a portion of the data summarized from the calculation for A.P. and three substituted A.P.'s. These calculations differ somewhat from previous tables of this kind we have given. The current ones are based on measured heats of formation obtained for us by Dr. G. S. Pearson of the British Embassy through the laboratory studies of Dr. Finch at Royal Holloway College. The values are given in Table VI. Enthalpies of solution in water were used to determine heats of formation.(9).

The numerical differences between A.P. parameters and those for methyl A.P. are striking and presage the large differences in combustion behavior that we have found.

TABLE I

AMMONIUM PERCHLORATE MONOPROPELLANT
COMBUSTION EQUILIBRIUM DATA

Heat of Formation (Enthalpy) -70.69 Kcal/mole
Initial Temperature 298.15°K
Density 1.95 g/cc

Pressure

<u>Parameters</u>	<u>1 atm.</u>	<u>34 atm.</u>	<u>68 atm</u>
Temp., °K	1375	1397	1403
Temp., °F	2015	2054	2066
Enthalpy, cal/g	-601.6	-601.6	-601.6
Entropy, cal/g - °K	2.212	1.960	1.911
Average Molecular Wt.	27.691	27.871	27.930
Heat Capacity cal/g - °K	0.351	0.364	0.367
Ratio of Specific Heats cp/cv	1.264	1.259	1.258

Combustion Species
Moles/100 grams

Cl	0.0054	0.0022	0.0019
HCl	0.8168	0.7301	0.7005
ClO	0.0001	0.0002	0.0002
Cl ₂	0.0144	0.0593	0.0742
OH	0.0002	0.0001	0.0001
H ₂ O	1.2937	1.3371	1.3519
NO	0.0011	0.0013	0.0013
N ₂	0.4250	0.4249	0.4249
O ₂	1.0546	1.0329	1.0254

Additional products which were considered but whose mole fractions were less than 0.000005 for all assigned conditions: H, NH, H₂, NH₃, N and O.

TABLE II
METHYL AMMONIUM PERCHLORATE, $\text{CH}_3\text{NH}_3\text{ClO}_4$
THERMODYNAMIC CALCULATIONS OF MONOPROPELLANT
COMBUSTION PARAMETERS

Heat of Formation, K cal/Mol - 67.82

Gas Parameters	Equilibrium Combustion Pressure (Atm.)		
	1	34	68
Temp., °K	2733	3024	3076
Mol., WT.	24.81	25.49	25.61
Heat Capacity, Cp, cal/g/°K	1.535	0.973	0.889
Gamma, Cp/Cv	1.119	1.141	1.146
lsp, lb. f. sec/lb. m.	252.3*	239.8**	256.3**
C Star, ft./sec.	4977	5118	5141
Gas Products, Mol. fr.			
Cl	0.030	0.016	0.014
HCl	0.159	0.177	0.180
CH_4	-	-	-
CO	0.092	0.084	0.082
CO_2	0.696	0.110	0.113
H	0.015	0.006	0.005
OH	0.029	0.020	0.018
H_2	0.059	0.046	0.043
H_2O	0.406	0.434	0.439
NO	0.003	0.003	0.003
N_2	0.093	0.095	0.096
O	0.005	0.002	0.001
O_2	0.014	0.006	0.005

* Expanded to 0.216 psia (1/68 Atm.)

** Expanded to 14.7 psia

TABLE III
TRIMETHYL AMMONIUM PERCHLORATE, $(CH_3)_3NHClO_4$
THERMODYNAMIC CALCULATIONS OF MONOPROPELLANT
COMBUSTION PARAMETERS

Heat of Formation, K cal/Mol - 65.91

<u>Gas Parameters</u>	<u>Equilibrium Combustion Pressure (Atm.)</u>		
	<u>1</u>	<u>34</u>	<u>68</u>
Temp., °K	1647	1649	1653
Mol. Wt.	17.73	17.74	17.76
Heat Capacity, Cp, Cal/g/°K	0.495	0.501	0.522
Gamma, Cp/C	1.293	1.292	1.268
Isp, lb. f. sec/lb. m.	210.6*	215.1**	216.5**
C Star, ft/sec.	4337	4334	4347
<u>Gas Products, Mol. fr.</u>			
Cl	-	-	-
HCl	0.111	0.111	0.111
CH ₂	-	-	0.001
CO	0.312	0.312	0.311
CO ₂	0.021	0.022	0.022
H	-	-	-
OH	-	-	-
H ₂	0.410	0.410	0.408
H ₂ O	0.090	0.090	0.091
NO	-	-	-
N ₂	0.056	0.056	0.056
O	-	-	-
O ₂	-	-	-

*expanded to 0.216 psia (1/68 atm.)

**expanded to 14.7 psia

TABLE IV

ETHYL AMMONIUM PERCHLORATE, $C_2H_5NH_3ClO_4$
THERMODYNAMIC CALCULATION OF MONOPROPELLANT
COMBUSTION PARAMETERS

Heat of Formation, K Cal/Mol - 72.10

Gas Parameters	Equilibrium Combustion Pressure (atm)		
	1	34	68
Temp., °K	2254	2281	2282
Mol. Wt.	20.73	20.78	20.79
Heat Capacity, Cp, Cal/g/°K	0.565	0.495	0.490
Gamma, Cp/Cv	1.221	1.244	1.245
Isp, lb.f. sec/lb.m.	231.7*	218.6**	231.9**
C Star, ft./sec.	4776	4775	4768
Gas Products, Mol. fr			
Cl	0.002	-	-
HCl	0.141	0.142	0.143
CH ₂	-	-	-
CO	0.242	0.243	0.243
CO ₂	0.043	0.042	0.042
H	0.004	0.001	0.001
OH	0.001	-	-
H ₂	0.255	0.256	0.256
H ₂ O	0.242	0.243	0.243
NO	-	-	-
N ₂	0.071	0.071	0.071
O ₂	-	-	-

*expanded to 0.216 psia (1/68 atm.)

**expanded to 14.7 psia

TABLE IV
DIMETHYL AMMONIUM PERCHLORATE, $(CH_3)_2NH_3ClO_4$
THERMODYNAMIC CALCULATIONS OF MONOPROPELLANT
COMBUSTION PARAMETERS

Heat of Formation, Kcal/Mol - 66.59

Equilibrium Combustion Pressure (atm.)

Gas Parameters

	<u>1</u>	<u>34</u>	<u>66</u>
Temp., °K	2319	2357	2359
Mol. Wt.	20.71	20.78	20.78
Heat Capacity, Cp, Cal/g/°K	0.598	0.503	0.497
Gamma, Cp/Cv	1.213	1.240	1.243
Isp, lb. f. sec/lb. m.	235.7*	222.5**	236.0**
C Star, ft./sec.	4860	4859	4848

Gas Products, Mol. fr.

Cl	0.002	-	-
HCl	0.140	0.142	0.142
CH ₄	-	-	-
CO	0.243	0.244	0.244
CO ₂	0.642	0.641	0.641
H	0.005	0.001	0.001
OH	0.001	-	-
H ₂	0.254	0.255	0.235
H ₂ O	0.242	0.244	0.244
NO	-	-	-
N ₂	0.071	0.071	0.071
O	-	-	-
C ₂	-	-	-

*expanded to 0.216 psia (1/66 atm.)

**expanded to 14.7 psia

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TABLE VI
STANDARD HEATS OF FORMATION*
OF ALKYL SUBSTITUTED AMMONIUM PERCHLORATES

Compound	ΔH_f° (298) Kcal/Mole
$\text{CH}_3\text{NH}_3\text{ClO}_4$	-67.82
$(\text{CH}_3)_2\text{NH}_2\text{ClO}_4$	-66.59
$(\text{CH}_3)_3\text{NHCLO}_4$	-65.91
$\text{C}_2\text{H}_5\text{NH}_3\text{ClO}_4$	-72.10
$(\text{C}_2\text{H}_5)_2\text{NH}_2\text{ClO}_4$	-80.56
$(\text{C}_2\text{H}_5)_3\text{NHCLO}_4$	-93.64
$(\text{CH}_2\text{NH}_3\text{ClO}_4)_2^{**}$	-110.61

* Data supplied by Dr. A. Finch.

** Ethylene diamine diperchlorate

We are now beginning to pay particular attention to the changes in these parameters as combustion takes place at 1, 34 and 68 atmospheres. We have already demonstrated the effects of chemical composition on burning rate. We are now anxious to probe into those chemical and physical factors affecting the slope of the rate-pressure curve. We believe slope might be related to the degree of shift in flame temperatures and product composition - as pressure is varied. Note that methyl A.P. is nearly stoichiometrically balanced for maximum heat release - and has wide variations in flame temperature and composition as pressure is varied. Trimethyl A.P., on the other hand, is a good bit removed toward the fuel side of optimum stoichiometry. It shows very little change in parameters with pressure. We want to determine whether it also has a much lower rate-pressure slope.

For the future we intend to manipulate computer programs to give equilibrium mixes of intermediary combustion products - at temperatures between the burning surface temperature - and the final adiabatic flame temperature. We want to get as many calculated and measured checks as possible on what is happening much nearer to the surface of a burning A.P. crystal.

V. Mass Spectrometer Analyses of Oxidizer Decomposition

During this period we have initiated both low and high resolution mass spectral studies of A.P. We consider these and further studies we plan to be the next most logical steps in clarifying AP combustion mechanisms. We are aware of the relatively low temperature and very low pressure operating aspects of mass spectrometry - as compared with conditions inside an operating rocket motor. However, we feel these studies will provide information to be pieced together with that from other experimentation and calculation.

One thing we feel is that products we find in the mass spectra, having been impacted with electrons, vaporized and reacted in their travel to the detector - would probably be able to exist for very short but important lengths of time at and near the solid surface - at rocket operating pressures. We intend to look for products that can provide a liquid-like surface, and that would have resulted from exothermic reactions. Identification of potential liquid surface products is essential to allow the mechanism to conform with the photographic findings of Price, Boggs and coworkers at China Lake. (10) Identification of a variety of possible porous surface exothermic reactions is important since over the last few years we have seen increasing evidence that there may not be enough heat transfer from the gas zone to the solid surface to keep the reaction self-sustaining.

A. Prior Work - Maycock(11) has described the importance of mass spectrometer source, sampling and analyses regions in influencing the kinds of data to be obtained for A.P. decomposition. Pellett (12)

has described the use of ruby and CO_2 lasers in the flash photolysis heating of A.P. to cause decomposition. His products were analyzed by time of flight as were Maycock's. Most investigators, other than Pellett, have used conduction heating of the A.P. sample to cause decomposition. Mack and Wilmot used cold-matrix isolation - infrared spectroscopy up to 180°C to trap A.P. decomposition products. Guillory and King (13) have investigated A.P. decomposition between 200 and 400°C , finding ClO_2 to be an important surface product. Guillory, Mack and King (14) have gone on to the substituted A.P.'s using the time-of-flight. Isotope tagged compounds like N^{15} have been used by a few investigators to help separate and identify species like NH_4 and H_2O that have similar masses.

B. Experimental Goals - We see that there are several types of problems facing us as we work to relate decomposition data to combustion models:

- 1) We must be able in some studies to simulate the combustion temperatures; i.e., 500° to 600°C at the solid, liquid or porous surface, and 1100°C in the equilibrium gas phase.
- 2) We must be able to predict the effects on the reactions of increasing pressure to several hundred atmospheres.
- 3) We must be able to relate electron impact cracking in the mass spectrometer to pyrolytic reactions in combustion.
- 4) We must apply methods like cold matrix trapping followed by Raman or EPR spectrometry in order to detect free radicals.

We intend to begin by making as complete specie analyses as possible using time-of-flight and high resolution spectroscopy- and

setting up reaction paths that will explain the findings. These results will be related to results of other investigators using other experimental conditions. Then we will begin using the modified ammonium perchlorates to learn the effects of hydrocarbon interactions with A.P.

C. Equipment and Experimental Procedures - A Bendix Model 12-101 time-of-flight mass spectrometer was used for these low temperature studies. Temperatures ranged from 80°C to 165°C. The sample probe molecular leak, and heating elements were constructed as described by Guillory (14).

The Typical Operating Conditions Were:

Ionizing current - 70 eV

Capture Sensitivity - 10^{-8} amps.

Sample heating rate was controlled by a Bendix Model 843 Hot Filament Sample Controller.

A typical run consisted of sample selection (approx. 5 mg to 20 mg); spectrometer preparation and run; and data reordering. A background scan is run immediately after pumping the system down to 10^{-5} torr. Heat was turned on to the sample and the cracking patterns continuously monitored until desired temperature was reached.

Where mass numbers were similar, species identity was finally determined on a Varian high resolution mass spectrometer.

D. Data and Analysis - Table VII presents the species found. Figures 6 through 10 show the relative abundances for species from nitrogen

TABLE VII

SPECIES DETECTED FROM SUBLIMATION AND CRACKING OF A.P.

<u>MASS/CHANGE</u>	<u>SPECIES</u>
14	N
16	O, NH ₂
17	OH, NH ₃
18	H ₂ O, NH ₄ ⁺
22	N ₂ , CO
30	NO
32	O ₂ , N ₂ , H ₄
35	Cl ³⁵
36	HCl ³⁵
37	Cl ³⁷
38	HCl ³⁷
44	CO ₂ , H ₂ O
51	Cl ³⁵ O
53	Cl ³⁷ O
67	Cl ³⁵ O ₂
69	Cl ³⁷ O ₂
83	Cl ³⁵ O
85	Cl ³⁷ O ₃
100	HCl ³⁵ O ₄
102	HCl ³⁷ O ₄

TIME-OF-FLIGHT MASS SPECTROMETER SCAN
 NH_4ClO_4 AT 80°C

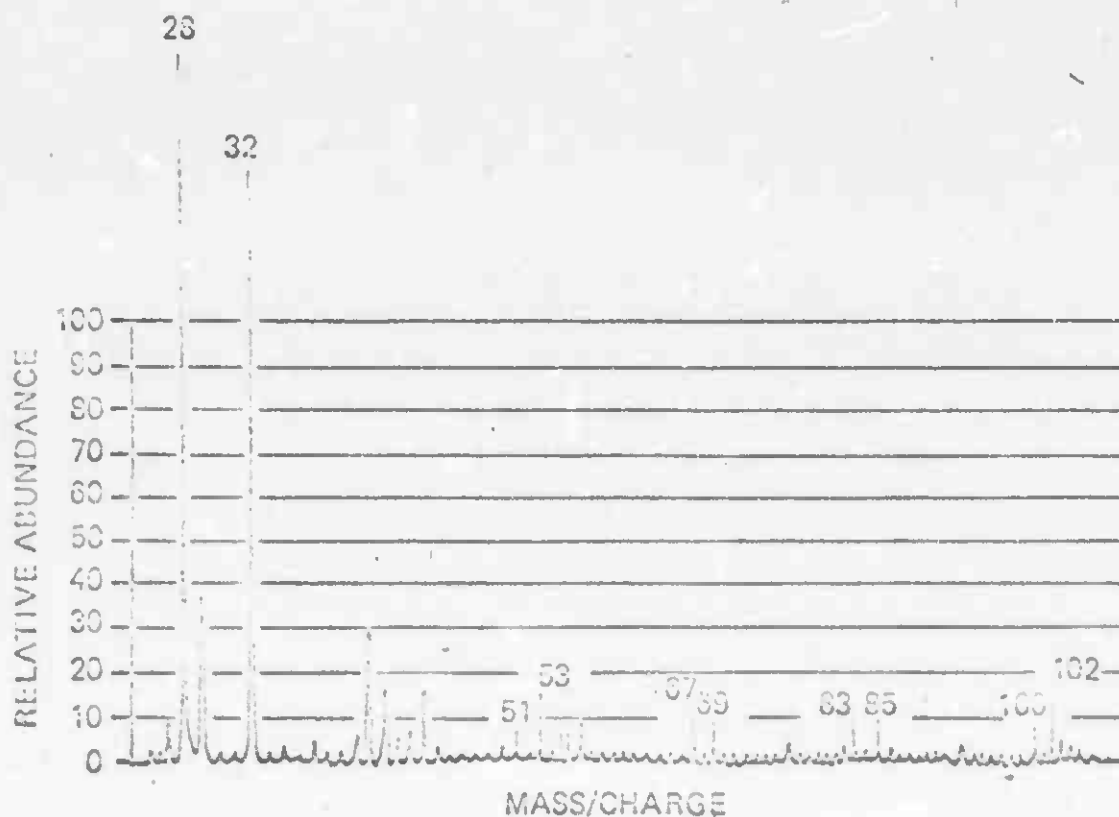


Figure 6

TIME-OF-FLIGHT MASS SPECTROMETER SCAN
 NH_4ClO_4 AT 95°C

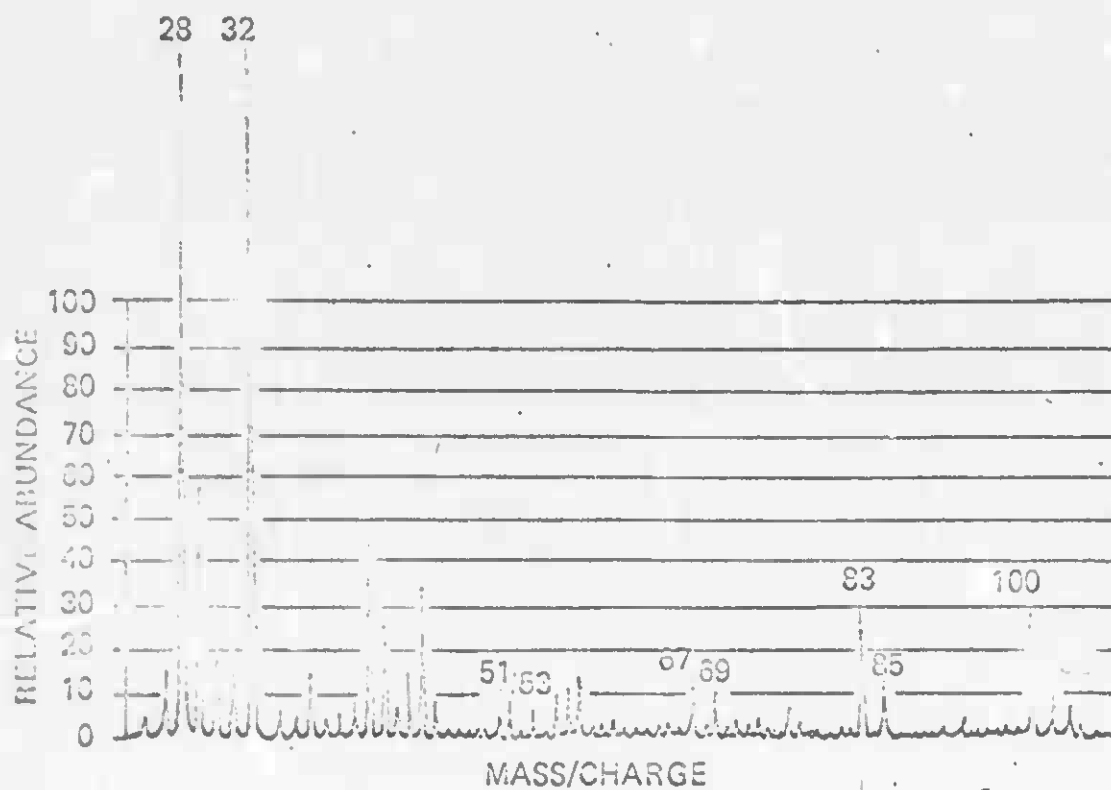


Figure 7

TIME-OF-FLIGHT MASS SPECTROMETER SCAN
 NH_4ClO_4 AT 115°C

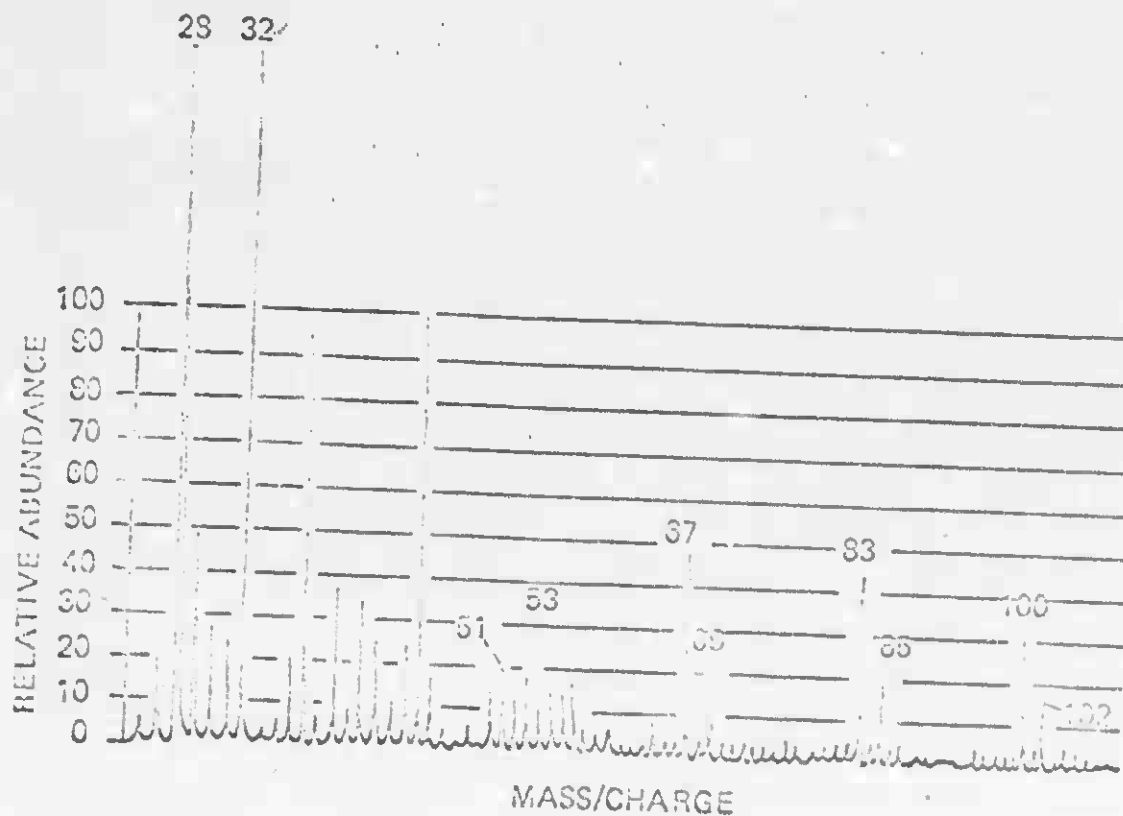


Figure 8

TIME-OF-FLIGHT MASS SPECTROMETER SCAN
 NH_4ClO_4 AT 135°C

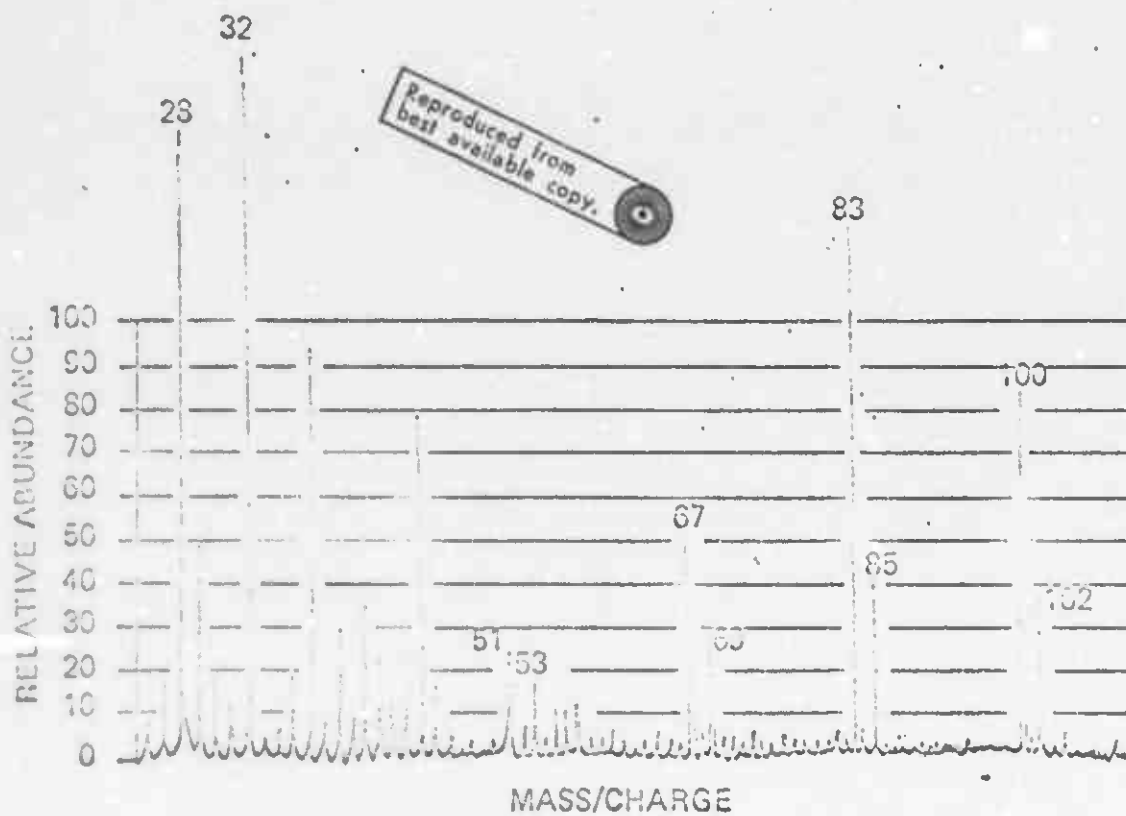


Figure 9

TIME-OF-FLIGHT MASS SPECTROMETER SCAN
 NH_4ClO_4 AT 165°C

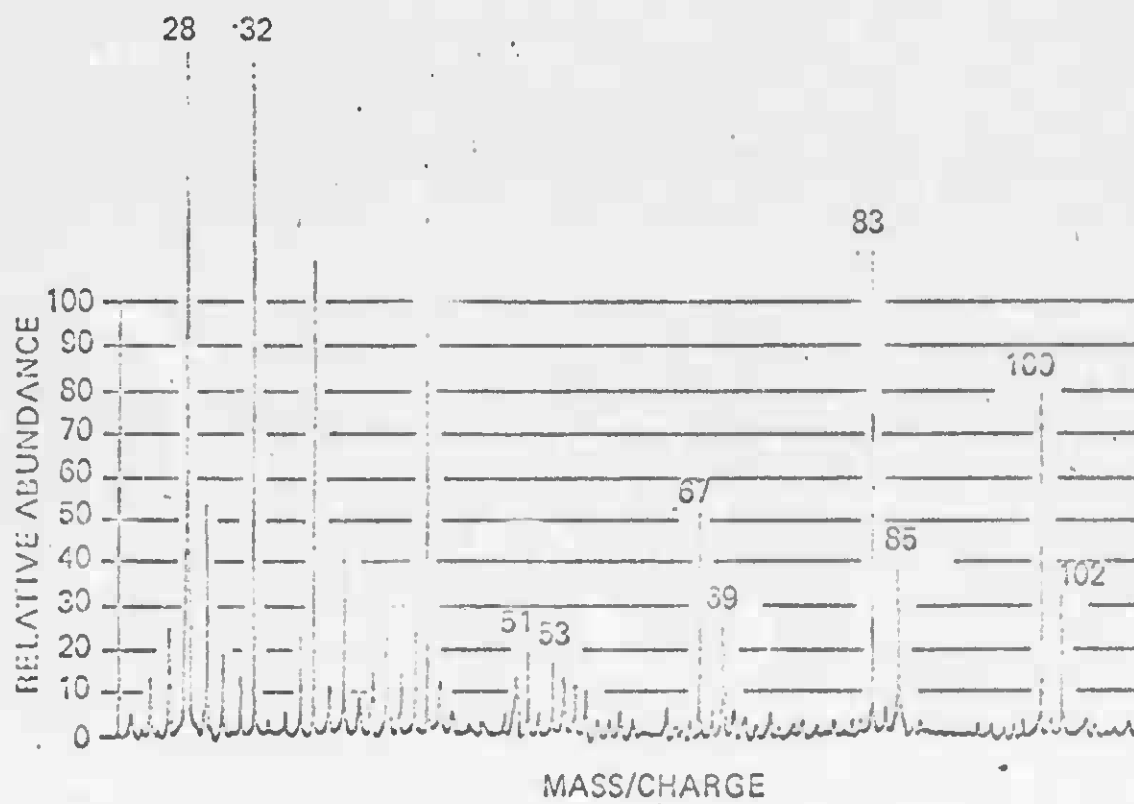


Figure 10

to perchloric acid; and at temperatures from 80°C to 165°C. In these studies we focused attention on the chlorine species.

In examining the table and spectrometer scans we find agreement with all other investigators, that there is no NH_4ClO_4 in the gas phase. In addition there is no ClO_4 found. HCl as shown by masses 36 and 38 was the most abundant chlorine specie-followed by ClO_3 , HClO_4 , ClO_2 and ClO . Cl was a minor specie and Cl_2 was not found. Absence of Cl_2 may be an artifact of the low pressure - as it is known to exist at about 1/10 the mole percent of HCl as a final product at 68 atmospheres. Most of the possible nitrogen species were found. Of particular interest was the presence of detectable amounts of NH_4 . We want to particularly follow this aspect further. It may be that the ClO_4 ion or the ClO_4 radical either were not formed in large quantity under these conditions; or that they further react so rapidly that none can be detected.

Since we found more ClO_3 than either ClO or ClO_2 , and sufficient OH to go with it, we are drawn toward the conclusion that:



In HClO_4 , the symmetry of the perchlorate ion is upset. The Cl-O bond, which was 1.408\AA for each of the oxygens, is lengthened to a Cl-OH bond length of 1.630\AA . This sets the stage for HClO_4 decomposition to ClO_3 and OH radicals. Chlorine trioxide is very unstable and decomposes bimolecularly to ClO_2 and O_2 . At any rate, it can be seen that the very reactive ClO_3 and OH radicals can readily form. This beginning reaction sequence, if accurate, can explain the rapid and stable burning of all oxidizers that can

decompose to give HClO_4 . We, of course, found considerable NH_3 and HClO_4 to confirm the widely accepted first step:



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We believe there is little doubt that this is an important reaction. However, as discussed above, we do not yet want to ignore the possibility of:



or



occurring under combustion conditions of much higher temperatures and pressures. We found so little ClO and no HCl , such that reactions that have been proposed like:



and



cannot have been very important under the conditions we studied.

Rather, our results would lead us toward



and



In other words, any reactions that could lead to HCl and O_2 , without involving ClO or HOCl ; and using hydrogens from NH_3 . In fact the hydrogens seem to readily strip off the nitrogen forming OH and H_2O with all available oxygen. However, somewhat analogous to not

finding ClO , is the absence of NH in our studies.

Our prior studies with deuterated A.P. (ND_4ClO_4) showed that its combustion reactions were no slower than those of A.P. From this we conclude that the NH_4 or NH_3 reactions are not rate limiting.

Table VIII shows the general order of reactions that would tend to explain our analytical findings. They are arranged in increasing numerical order to indicate roughly what we believe to be earlier and later reactions.

Table IX shows several reactions that are not supported by our findings.

Earlier studies of other investigators have shown that, at the temperatures we have studied, purely thermal input to ammonium perchlorate, followed by rapid trapping, would lead to chiefly perchloric acid and ammonia. The additional products we have found are largely due to electron cracking. By varying temperatures and electron energies, however, we should be able to relate the two effects.

TABLE IX

TYPICAL NONJUSTIFIED A.P. DECOMPOSITION

REACTION STEPS



VI Oxidizer Combustion Experiments

The screening test for combustion rates of new compounds used in this laboratory is the soda straw burning of the pure powdered material. The precautions used to achieve reproducible results have been described in past reports(2) Table X presents the results of testing ten perchlorates; starting with A.P. Good rate data was obtained for all but tetramethyl A.P. We believe its difficulty is twofold. First it is a quaternary ammonium salt and has that family's high crystal stability. Secondly, it cannot readily decompose to produce perchloric acid. Most investigators are now convinced that inability to form perchloric acid interferes greatly with the ultimate liberation of the powerful chlorine oxides. We hope to show these decomposition differences by mass spectrometry.

Tetrabutyl ammonium perchlorate did burn, but showed the slowest rate of all the perchlorates. It is far on the fuel-rich side of stoichiometry.

It can be seen that dimethyl ammonium perchlorate is the fastest burning of the simple alkyl substituted ammonium perchlorates. This is surprising because the dimethyl compound is not at the optimum fuel ($R_n NH_{4-n}$) oxidizer (ClO_4) balance point for maximum energy release and flame temperature. We are, therefore, led to theorize that although fuel/oxidizer balance is generally of greatest importance, in this case the weakening of ionic nature in going from methyl to dimethyl A.P. has overshadowed it. The lower crystal stability to thermal energy - as shown by the slightly lower DTA exotherm -

and only one endotherm to absorb energy - causes dimethyl A.P. to actually burn faster.

The more complicated diperchlorates shown below the solid line, ethylene diamine diperchlorate and piperazine diperchlorate, are the fastest burning perchlorates we have found. We are still investigating the adiabatic combustion temperatures and products but believe they are no higher than methyl A.P. It does look like the ability to form methylene or ethylene radicals as compared with methyl or ethyl is important.

Methyl A.P. was chosen as the starting material for propellant burning rate tests.

TABLE X

OXIDIZER POWDER BURNING RATES*
AMMONIUM PERCHLORATE SERIES

$R_n NH_{(4-n)} ClO_4$	$r, \text{ IN./SEC}$
$NH_4 ClO_4$	0.033 (9.35 @ 1000 PSI)
$CH_3 NH_3 ClO_4$	0.103
$(CH_3)_2 NH_2 ClO_4$	0.132
$(CH_3)_3 NH ClO_4$	0.065
$(CH_3)_4 N ClO_4$	QUENCHES
$CH_3 CH_2 NH_3 ClO_4$	0.087
$CH_3 CH_2 CH_2 NH_3 ClO_4$	0.077
$[CH_3 (CH_2)_3]_4 N ClO_4$	0.027
$[H_3 N CH_2 CH_2 NH_3] [ClO_4]_2$	0.148
$ \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 \\ \diagdown \quad \diagup \end{array} [ClO_4]_2 $	0.203

(*AT AMBIENT CONDITIONS IN COMBUSTIBLE TUBES, 4MM I.D. AND
-40+50 MESH DRIED POWDER)

VII Propellant Burning Rate Confirmation

Once it was determined that the combustion differences between ammonium perchlorate and the substituted ammonium perchlorates were real and reproducible in the powder burning screening test, propellant burning rate tests were planned. Since many laboratory tests of propellant burning rate have given non-reproducible results because of poor choice of propellant system, improper fabrication of propellant strands and inadequate testing, special care was taken in each of these areas.

The propellant formulation chosen as a control was:

<u>Composition</u>	<u>Wt. %</u>
Polymeric binder	15.0
Aluminum powder	10.0
Ammonium perchlorate	
2 micron particle size	36.80
15 micron particle size	22.00
180 micron particle size	<u>16.20</u>
	100.00

This formulation has a burning rate at 2000 psia of 1.20 in/sec. It is balanced to give maximum practical content of A.P. and aluminum. The aluminum provides combustion stability. The higher the A.P. content, and the finer the A.P. particle size, the higher the burning rate. However, the limit of the liquid polymeric binder's ability to wet all solid particle surfaces - and thus to be able to mix properly with the solids and provide homogeneity - is reached at approximately the A.P. content, and particle sizes shown.



When proper care is not given to these factors, propellants containing voids, and subject to cracking during combustion testing result. This leads to high and nonreproducible burning rates.

The strands prepared for this testing were cured propellants. They were x-rayed prior to test, and any void containing sections were discarded.

The polymeric binder used was a standard carboxyl terminated polybutadiene polymer, epoxide cured with cure catalyst assistance, and containing 2% plasticizer. The aluminum powder used was Reynolds H-5.

The most practical current method of increasing the burning rate of the control propellant is the introduction of iron compounds substituted for a few percent of the coarsest oxidizer fraction. When more than two or three percent of these compounds are used, the incremental increase in burning rate becomes very small, and rocket performance begins to suffer from the high molecular weight of the iron combustion products.

Generally a blend of iron oxide and substituted ferrocenes gives the best effect, while partly avoiding the relatively high vapor pressure of Ferrocene itself. Ferrocene tends to migrate within the cured propellant mass- and actually to vaporize from exposed surfaces. Unfortunately, even the substituted ferrocenes migrate somewhat - however, they are superior in catalytic effect to iron oxide, apparently due to the better utilization of atomic iron and its oxides by their release in an activated state when the hydrocarbon portions of the ferrocenes burn.

While the control propellant has a burning rate of 1.2 in/sec at 2000 psia, substitution of 2% Fe_2O_3 for 2% of the A.P. (180 micron fraction) gives a propellant with a rate of 1.8 in/sec. Substituting a blend of iron oxide and substituted ferrocenes can raise the rate to 1.9 to 2.0 in/sec.

To test the effect of methylammonium perchlorate, two levels of substitution in the control formulation were used: replacement of 2% of the 180 micron A.P. with MAP, and replacement of all of the 180 micron A.P. fraction with MAP. The several control and test formulations are given in Table XI together with the strand burning rates at 2000 psia. All strands were burned under dry nitrogen. The fact that the 2% substitution of MAP for AP gives little burning rate effect indicates that MAP is not producing a catalytic effect like that of the iron compounds. The fact that substantial substitution of MAP for AP produces more than a doubling of burning rate shows that MAP's intrinsically faster burning rate properties do carry through to increase propellant burning rate.

Further testing will delineate the practical limits of MAP substitution for A.P.

TABLE XI
PROPELLANT FORMULATIONS AND BURNING RATE RESULTS

<u>Composition</u>	<u>Weight Percent</u>			
	<u>Control</u>	<u>Fe₂O₃ Catalyzed</u>	<u>Mixed Iron Catalysts</u>	<u>MAP Substitution Low High</u>
Polymeric Binder	15.0	15.0	15.0	15.0 15.0
Aluminum Powder	10.0	10.0	10.0	10.0 10.0
Ammonium perchlorate				
2 micron	36.8	36.8	36.8	36.8 36.8
15 micron	22.0	22.0	22.0	22.0 22.0
180 micron	16.2	14.2	14.7	14.2 0.0
Methyl Ammonium				
Perchlorate (180 micron)	0.0	0.0	0.0	2.0 16.2
Iron Oxide	0.0	2.0	0.5	0.0 0.0
Ferrocenes	0.0	0.0	1.0	0.0 0.0
	100.0	100.0	100.0	100.0 100.0
Strand burning rates				
at 2000 psia	1.2	1.8	1.9	1.3 2.7
(in/sec)				



VIII Combustion Theory and Model Improvement

For many years considerable applied effort has been devoted to the problems of making much faster and much slower burning propellants. Also a great deal of effort has been expended to improve ignition reliability of rocket motors, lengthen their storage life, increase their factors of safety in handling and manufacturing, and finally to be able to quench solid propellant motors and then reignite them on command. All of these efforts have suffered from the inability to specify in a clear stepwise fashion what happens chemically and kinetically when ammonium perchlorate, and its propellants are subjected to thermal energy. This research at the University of Delaware is specifically designed to provide new data so that more direct methods of solid rocket motor control may be developed.

In developing more rational theory and models it will be useful to establish pressure ranges of interest and delineate the kinds of discrete zones that are present. We then want to assign dimensions and temperatures. Finally, we want to specify reactions, rates, and products within the zones.

A. Solid Phase Reactions

Considerable discussion has been generated over the past few years about the relevance of laboratory thermal analyses to combustion phenomena. Those decomposition studies are conducted at somewhat lower temperatures, over far longer time periods, and generally at lower pressures than the conditions used in rocket propulsion. One major goal we have is to give quantitative explanations of the importance of solid phase reactions on combustion.

It is our belief that laboratory methods, like: DTA, TGA, DSC and various methods of isothermal decomposition, will each provide important bits of information in filling out the overall picture. They may have greatest applicability to the phase change taking place beneath the crystal surface and the decomposition processes taking place in the porous zone that appears to extend between 10 and 1000 microns down into the condensed phase during combustion. The second concern of our research is clarification of what is happening at the interface between the combustion gases and the porous solid or melting zone for a burning crystal of ammonium perchlorate. A melt-like zone occurs on the crystal surface, especially during low pressure combustion. In addition, this effect is much stronger with added impurities like potassium salts. The potassium compounds probably form lower melting eutectics which then boil away from the surface. It is also believed that chloride and chlorate impurities cause strong effects. The photographs of crystals that have been quenched during burning show the formation of these melts. The high speed, high magnification movies of crystal burning at pressures up to about 6,000 psi, taken by Boggs and Price have amply shown this effect. We need to provide better chemical explanations for the effects seen in these movies. We also know that where the existence of surface melts has been definitely proved, and these melts are present in larger proportion than in pure A.P., the combustion is strongly affected. Hightower and Boggs have shown that burning becomes very erratic as globules of the melts coalesce and then break away or vaporize from the surface. Under these conditions,



energy transfer is complicated. There are two different condensed phase reaction domains; one, in the melt, and one at the porous zone beneath. The presence of the melt, therefore, is a serious complication in analyzing the reaction mechanisms.

However, again from these films we know that somewhere above 2000 psi, and especially above 4000 psi, the melting becomes almost insignificant and burning becomes much more steady. These higher pressures are of greatest interest in the current efforts to produce very high burning rates. The porous zone in these cases is between 100 and 1000 microns thick, with the solid material being an array of long cylinders-mostly with their axes parallel to the burning axis.

B. Gas Phase Reactions

Now in addition to the change in the surface character, there is a pronounced change in the character of the gas phase. This phase is the third major concern of our proposed research. At the lower pressures there are various vapors visible and either no flame at all, or else a light blue flame. However, in the 2,000 to 4,000 psi range (again from the NWC films) a definite bright orange flame appears and it establishes itself much closer to the surface than the light blue flame. Since our combustion equilibrium calculations show very little difference in flame temperature when the pressure is varied from ambient pressure to over several thousand psi, we know that there is difficulty in correlating visible flame characteristics with calculated flame temperatures at lower pressures. We assume that combustion must be incomplete within the near flame zone at the lower

pressures. It has been known for some time that there have been many cases of rocket combustion inefficiency at pressures around 500 psi; and this might be part of what we are seeing in the low pressure A.P. combustion.

We are most interested in being able to understand effects in the pressure regime most important to propulsion, and the one which can be more readily modelled. We will, therefore, focus on studies in which the adiabatic gas phase calculations of temperatures and reaction products are applicable, and studies in which the reaction is taking place at a porous solid surface with the products going directly to the gas phase. We will, therefore, be studying what happens when crystalline ammonium perchlorate is struck by radiant energy of high intensity, and thermal energy by gas conduction. Under these circumstances we will be most interested in detecting all of the initial decomposition products, and particularly finding out whether or not radicals such as ClO and OH exist as important species.

To better describe the important energy transfer modes, from gas to solid surface, we will be analyzing first the gas phase radiation in the infrared region that is striking the crystal surface; and secondly gas-solid thermal conduction. This radiation when it is from a combustion gas zone is far from black body radiation, and in fact the assumption of gray body radiation is even very poor. What we want to calculate, then confirm with measurements, is the spectral radiation from just above the visible up to about 8 or 10 microns. The peak energy transfer is undoubtedly in the 1 to 3 micron infrared wave band. We would expect the ultraviolet to have little

importance unless we study metallized propellant flames. We must then determine how the crystalline structures of a family of oxidizers can absorb specific regions. Thermal conduction calculations can be rather straightforward if we can correctly specify temperatures at various stations within the solid and gas phases. Good estimates have been made by others already of solid surface and subsurface temperatures--but the gas phase temperatures--and gradients near the surface are only poorly understood.

C. Initial Combustion Products

Among the literature of A.P. decomposition and combustion, there are a number of references dealing with overall reactions like:



It is important that we fully understand what has been predicted and formed in these circumstances so that we can attack the preliminary or initial steps more intelligently.

For example Simchen (J. Appl. Chem., 1963 13 369) calculated the equilibrium gas composition for zero pressure:



and for high pressures:



It was assumed that any given combustion pressure would then give compositions between these extremes. In fact Chosel (Aerojet report 372-01F March 15, 1965) has proposed the following empirical equation, in which the terms a and b represent the

experimental values determined for HCl and N_2 respectively, and are related to c by the expression:

$$a+b+c=2/3$$

The equation is:



It has been found to be in excellent agreement with experimental values.

Earlier in this report, we have tabulated data on the calculated combustion species for A.P. combustion at atmospheric pressure, and at 34 and 68 atmospheres. There was general agreement with Cheselke's data - and good agreement with Simchen's "high pressure" data (when comparing with the University of Delaware 68 atmosphere data). Simchen's "zero pressure" data differs considerably from our one atmosphere data...indicating the great importance of carefully specifying pressures, when working in very low pressure combustion. Possibly the best practical check of the computer generated species, temperatures, etc. is that of the thousands of calculations that have been made of propellant specific impulse, practically all have checked within a few percent of the measured values derived from the impulse generated during test rocket firings.

The data shows that in the equilibrium flame such active species as ClO_x and OH are practically nonexistent for A.P. or its homologs. However, we are more interested in the initial reaction taking place far closer to the crystalline surface...say within one to ten microns.

In searching for the critical first steps in the combustion of A.P. and A.P. propellants, we believe that mass spectroscopy holds promise as a combustion simulant and as an analytical tool when used with pure and substituted ammonium perchlorates. Various methods of radiant and hot gas heating should be compared with the results of mild sample heating and electron bombardment. We are also interested in the kinds of radicals that pyrolysis produces with hydrocarbons, and their interaction with ClO_x and OH. We would expect CH_3 , CH_2 and CH to be readily formed at the extremely high combustion temperatures. In our substituted A.P.'s, we essentially have one unit of "binder" in each unit cell. Now the particularly fast burning of these compounds is due to at least three factors; 1) weakened crystal forces providing a more ready release of HClO_4 , 2) the addition of the active CH_3 radicals to the combustion process, and 3) the higher local flame temperature due to much higher heat release because of the fuel/oxidizer balance.

D. Determination of Combustion Zone Radiation Effects on Propellant Burning Rate

In the study of single ingredient and composite propellant burning rates, the importance of radiation transfer from the hot combustion zone to the solid surface has not been made clear as yet. Although for years it was thought that only sublimation of A.P. occurred at the surface, recent studies indicate the possibility that some exothermic reactions are taking place at the solid surface. However, we know that in arc or laser ignition of propellant, all energy input to the surface, at least initially, is radiation. At

the usual combustion temperatures, the major part of thermal radiation takes place in the wavelength region between about one and ten microns. It has been shown (15, 16) that the gaseous products in the much thinner reaction zone (first gaseous zone above solid surface) would probably have very little effect on the overall radiation picture. They also showed that for all practical sizes of strands, only about 1/20th of the flame zone radiation energy could be striking the surface. This calculation was applicable to combustion pressures of 25 and 300 atmospheres. This fact in itself makes it hard to understand why propellants burned as strands in a strandburner, and propellants burned in a rocket motor, can have burning rates so nearly the same. It would seem that in long cylindrical, central perforate, solid propellant rocket motors there would be almost no radiative loss since practically all of the solid surface sees only the flame zone. In the strandburner, on the other hand, almost all (19/20ths) of the radiative energy should be lost to cool surroundings. From these and numerous other studies, we know that radiant energy transfer balance (losses vs. gains) is critical to the stable burning of strands of ammonium perchlorate below 300 psi. Uninsulated strands normally would not burn below 300 psi, but have been made to burn down to atmospheric pressure when additional radiant energy is supplied by an outside source; like an arc or laser. Also, insulated strands that can conserve thermal energy, burn below 300 psi. Our studies during 1966-1969 have shown that granular A.P. loosely loaded into sample tubes will burn stably and reproducibly down to 14.7 psi. We believe this can happen largely due to the fact that the oxidizer burns as a zone, and the portion of the zone below the

gas-solid surface interface conserves radiant energy. The excellent studies by Penner and Williams that are referenced above were conducted when data only from ammonium perchlorate was available. Since we now have available a series of perchlorates and nitrates with widely different chemical composition, and flame temperatures ranging from about 1000°K to 3000°K, we believe that far greater information about the influence of chemical composition on radiation and burning rate can be determined.

The following are steps in the basic investigational approach being followed:

1. We can calculate with confidence the equilibrium concentrations of the combustion products (flame zone composition) at their respective flame temperatures. (17)
2. Then, using the spectral emissivity characteristics for these products we can determine the wavelengths in which significant amounts of thermal energy will be radiated to the solid surface.
3. Using IR absorption curves and/or fundamental vibration, bending, etc. frequencies, for the pure solid compound, we can find those wavebands in which the solid compound is capable of absorbing energy.
4. Then, by matching the two sets of wavebands and knowing the radiance from the combustion flame in watts per square centimeter (using references 1 and 2 and the calculations above) for the given bands, we will have an estimate of the relative amount of energy that can be transferred into the solid surface that is undergoing combustion.

In a preliminary set of calculations using a simplified model, the flame zone was treated as a black body and the relative ability of several compounds to absorb energy from black bodies at their own flame temperatures was calculated. The data is given in Table XII. It can be seen from this table that there is some correlation between the "relative energy received" value and the burning rate. In fact the lowest energy received value was for tetramethyl ammonium perchlorate, and that compound does not burn as a monopropellant in our tests. Although the tetramethyl A.P. flame temperature is the lowest of the components examined, it is only 125°K below that of ammonium perchlorate; which burns steadily. This fact, plus the fact that methyl AN has a higher flame temperature than A.P., and yet only burns half as fast, shows that relative energy received is a better indicator of burning rate than flame temperature. The relative energy received value for the tetramethyl compound was only about 40% of that of the slowest of the other three compounds. This might indicate that there is just not enough energy being radiated to the surface to feed the endothermic decomposition reactions that precede sustained combustion. In looking at the IR absorption spectra for the tetramethyl compound, it is immediately seen that the lack of an N-H band in this compound removes the ability to absorb energy at about three microns. There is far more radiation available in this wavelength than at longer wavelengths. In fact the peak wavelength for radiant energy is between one and two microns. Also, it can be seen from the IR curves that the N-H absorption for methyl ammonium nitrate is rather weak in comparison to the perchlorate compounds. There is also nothing to compensate for

TABLE XII

Relative Radiant Oxidizer Burning Rates Vs. Relative Radiant Energy Factor

	1)* Flame Temp. (°K)	2)* Total Radiance (watts/cm ²)	3)* Absorption (%)	4)* Radiation (%)	5)* Relative Energy Rec'd (Watts/cm ²)	6)* Burnin Rate (in/se does n burn
Perchlorate Tetramethylammonium (CH ₃) ₄ NClO ₄	1277	15	75	3.5	.039	
Methylammonium nitrate CH ₃ NH ₂ NO ₃	1520	30	25	14	1.05	0.018
Ammonium perchlorate NH ₄ ClO ₄	1403	21.5	65	8.5	1.19	0.033
Perchlorate Dimethylammonium (CH ₃) ₂ NH ₂ ClO ₄	2139	112	45	10.5	5.94	0.132

* Column Explanations:

- 1) Calculated adiabatic flame temperature
- 2) Total energy radiated per square centimeter of surface from a black body at temperature shown in column 1)
- 3) Average percent intensity of absorption peaks for the solid compound in the IR region
- 4) Percent of total black body radiation falling in the peak regions represented by the percentages in column 3.
- 5) Multiply column 2) by columns 3) and 4) in their decimal equivalents
- 6) Oxidizer powder, -40 + 50 mesh, burning rate in sample tubes under ambient conditions.

the lack of the strong perchlorate absorption in the 8.5 to 10 microns region. Methyl ammonium nitrate is one of the slowest burning compounds tested. It may be that the presence, even though small, of an absorption band at the two to three micron region is the significant factor in allowing combustion to take place at all.

These are only preliminary conclusions from relatively rough calculations. They neglected the specific radiation bands for the combustion products, treating them as a black body. The whole problem will be adapted to computer solution because of the otherwise tremendously complex problem of matching emission curves for complex mixtures with the absorption curves for given compounds so that a "relative energy received" value can be obtained.

It is anticipated that this kind of a correlation, that is relative energy received versus burning rate for a range of chemical compounds might prove to be the strongest correlation of high temperature factors to burning rate.

We still believe that there are lower temperature factors that will effect what happens to the absorbed energy at the solid surface. However, we believe that differential thermal analysis, which describes the thermal response of the solid compound from ambient temperature up to the fast exothermic combustion point will provide these analyses. In the DTA analyses, we will be looking for the temperatures and sizes of endotherms, and the temperature of the final exotherm.

It is then believed that the proper combination of the high temperature radiation characteristics, and the lower temperature DTA characteristics, will give a far better explanation of why AP has the burning rate that is its characteristic; and what the chances

are of altering it by practical measures.

E. Determination of Combustion Zone Conduction Effects on
Propellant Burning Rate

It has long been assumed that the majority of the energy sustaining combustion of propellants was provided by conductive heat transfer from the combustion gases to the solid surface. This may well be so. However, the exact or even approximate quantity has always been in doubt due to our inability to specify temperatures at various stations in the combustion gas phase. We all know how hot the equilibrium gases are for A.P. We also know that they reach that temperature for sure some 500 to 1000 microns above the surface. But the real question is: at what minimum distance above the surface do the gases reach the 1400°K equilibrium temperature.

During 1971 we intend to begin calculating minimum distances that would give the acceptable amount of heat transfer under two conditions. The first is with no generation of heat at the surface; that is the surface reaction is totally endothermic, sublimation decomposition generating ammonia and perchloric acid gases. The second is with limited exothermic breakdown at the surface. We also intend to conduct equilibrium thermodynamic calculations for selected gas species--so we can find what products would be in the gas phase at temperatures less than the final combustion temperature. These calculations should be especially valuable in establishing temperature stations in the gas phase.



Herzberg (12) has discussed the earlier theories of Von Elbe relating to possible cellular flame structure within the ammonia perchloric acid flame. The ideas of Von Elbe should be pursued further in light of the availability of a wide variety of stoichiometrically balanced and imbalanced oxidizers for experimentation.

IX

Conclusions

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1. A new approach to high burning rate propellants is through use of monopropellant crystalline oxidizers having hydrocarbon containing cations.
2. The alkyl substituted ammonium perchlorates are excellent examples of this class of oxidizers.
3. Study of the reactions of these materials - in comparison with those of pure A.P. - provides capability of unlocking more of the secrets of AP combustion mechanisms than heretofore possible.
4. Mass Spectrometry of decomposition products at various temperatures combined with equilibrium calculations of combustion products, is providing data on intermediary combustion reactions.
5. A.P. samples exposed to less than 200°C, and 70 ev electron, start decomposing as follows:



6. ClO and NH are probably not formed.
7. Some NH_4 is found, but no ClO_4 .

X Future Work

1. Continue mass spectral studies of A.P. to get better measures of relative quantities of species produced.
2. Initiate mass spectral studies of substituted ammonium perchlorates.
3. Propose reaction mechanisms based on 1. and 2.
4. Establish single crystal combustion model with appropriate zones or regions specified.
5. Calculate zone temperature and energy transmission pathways.
6. Calculate intermediate temperature and end product equilibrium species for the gas phase.

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